CHARACTERIZATION OF HELLENISTIC PERIOD MEGARIAN BOWLS FROM DORYLAION

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The excavation works being carried out since 1989 at Dorylaion (Eskişehir/Turkey) results in many findings belonging to different civilizations spanning from the First Bronze age to Ottoman period. One of the important groups of these findings is the moldmade bowls, familiarly known as the Megarian bowls from the Hellenistic period (330-30 B.C.). In a frame of an archaeometry project work, these artifacts were characterized with different analytical techniques. Wavelength dispersive X-ray fluorescence (WDXRF) and X-ray diffraction (XRD) were used to study chemical and mineralogical composition of the bodies. Thermogravimetric-differential thermal analyses (TG-DTA) were performed to make the estimation of firing temperature of the sherds. Scanning electron microscopy (SEM) and energy dispersive X-ray spectrometry (EDX) were performed for the microstructural and microchemical characterization of body and slip layers of the selected potsherds. Based on the analyses results, the bowls should have been prepared from carbonated and siliceous clays and fired at the temperatures from 600 to 1000 °C. They have also iron-rich slip layers with different colors indicating probable adjustment of the redox conditions during firing. In addition, the effect of maximum firing temperature on microstructural characteristics was evaluated.

INTRODUCTION

Many civilizations lived in Anatolia during different historical periods. In this respect, archaeological excavations have still been carried out at different locations in Turkey. Amongst these locations, the ancient city Dorylaion excavation site, which is located about 3 km to the north-east of Eskişehir/Turkey (Figure 1), is the scope of this paper.

Dorylaion is a mound having 18 m height and 450 m diameter. According to the historical sources, this was a Phrygian city founded by Doryleos from Eritrea. It is called as Şarhöyük today. Dorylaion was located at the junction of the important roads of the central Anatolia leading to Marmara Sea, Aegean coast and the Mediterranean region. The first archaeological excavation in Dorylaion was carried out from 1989 to 1992 by a team from the Archaeology Department of Anadolu University/Turkey. Since then, regular excavations have been continuing to bring to light a wide variety of materials revealed from the different cultures of Ottoman, Byzantine, Roman, Hellenistic, Classical Phrygian, Hittite and First Bronze Period.

During the excavation of Dorylaion, the Hellenistic ceramic wares cover the large amount of findings. Amongst these findings, Megarian bowls (molded wares), a distinctive type of Hellenistic vessels, were uncovered as well, which were produced as semi-spherical shape with no pedestal by forming in moulds with plant or figurative relief decorations. It is known that these wares were famous around the Mediterranean basin during the Hellenistic period [1].

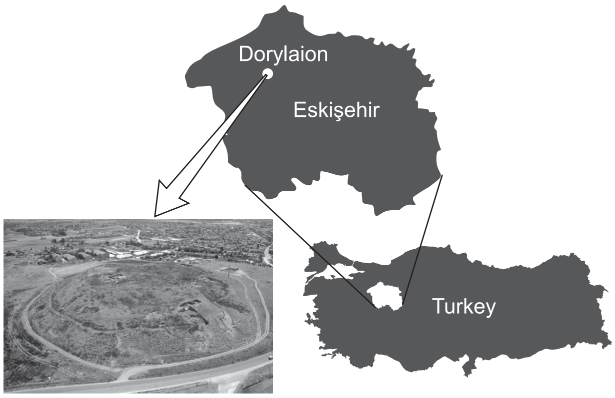


Figure 1. The location of Eskişehir (Turkey) and Dorylaion which is called as “Şarhöyük” today.

This study focuses the characterization of selected potsherds of Megarian bowls from Dorylaion with specific analytical techniques. Firstly, wavelength dispersive X-ray fluorescence (WDXRF) and X-ray diffraction (XRD) techniques were employed to study the chemical and mineralogical composition of the samples. Secondly, scanning electron microscopy (SEM) and energy dispersive X-ray spectrometry (EDX) were performed for the microstructural and microchemical characterization of the body and slip layers of potsherds. Thermogravimetric-differential thermal analyses (TG-DTA) were also performed to make the estimation of firing temperature of the sherds.

EXPERIMENTAL

Twenty representative Megarian bowl sherds (designated as M) were selected for the investigation (see Figure 2). For sample preparation, fine powders were prepared in an agate mortar after abrading the slip layers of the potsherds for the analysis by wavelength dispersive X-ray fluorescence (WDXRF) and X-ray diffraction (XRD) techniques. The tablets for WDXRF measurements were prepared by mixing the sample with $Li_2B_4O_7$ at the ratio 1:10 (by weight). Rigaku ZSX primus instrument was used for chemical analysis of major and minor elements. Rigaku Rint 2200 powder diffractometer with Cu Kα radiation was employed for XRD measurements. XRD patterns were obtained by scanning 5° to 70° 2Θ, with a goniometer speed of 2°/min, operating at 40 kV and 30 mA. Thermal analyses (TG-DTA) were performed with the powders of the sherds from room temperature to 1200°C in oxidation atmosphere. The firing temperature was increased by a rate of 10°C/min. Netzsch 409 Lux instrument was used for the analyses. Zeiss Evo 50EP (SEM) attached to an Oxford instruments (EDX) was used for microstructural investigation. Before the SEM investigation, the samples were polished and coated with Au/Pd target material to obtain flat and conductive surfaces.

Figure 2. The images of some of the Megarian bowl sherds.

RESULTS AND DISCUSSION

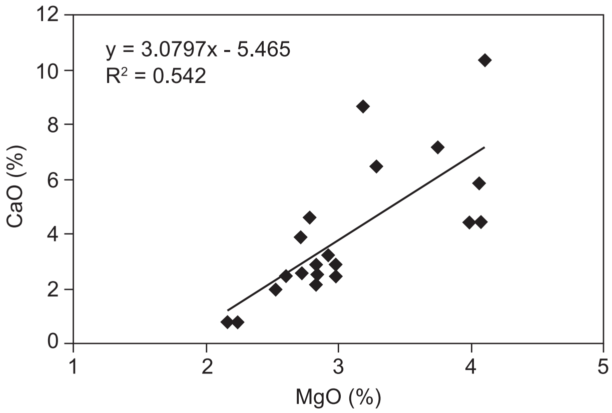
Chemical and Mineralogical Analysis

Chemical composition of major, minor and trace elements is important for provenance studies. These elements can act as the fingerprints of the raw material sources for production. Several instrumentation techniques can be employed such as optical emission spectrometry (OES), X-ray fluorescence (XRF), neutron activation analysis (NAA), particle induced X-ray emission (PIXE), atomic absorption spectrometry (AAS) and inductively coupled plasma (ICP) [2]. This study focuses the technological conditions of the potsherds preparation. Therefore, WDXRF analyses of the sherds were performed in semi-quantitative scale and trace elements in ppm amount were not considered in this study. The similarities and differences of the sherds in major and minor scale of elements and relations to mineralogical content were discussed. According to the WDXRF results, samples have various chemical compositions related to the raw materials used for the production. Especially, variations in SiO_2 and CaO contents are important for the indication of siliceous and calcareous mineralogical assemblages used for bodies. Some of the samples have high amount of CaO but some of them are poor. Therefore, the results were mentioned with two groups: calcium rich and calcium poor compositions. Representatively, three of the examined sherds with WDXRF are of from the calcium rich group and the other non calcareous sherds are given in Table 1.

Table 1. WDXRF results of the selected Megarian body sherds.

Oxide (wt.%)	Experimental code					
	Calcium rich			Calcium poor		
	M16	M4	M8	M7	M10	M20
SiO_2	55.65	55.09	51.90	57.07	57.04	60.57
Al_2O_3	18.73	19.06	19.08	23.81	23.68	20.45
Fe_2O_3	7.63	8.14	6.88	9.11	9.02	6.73
MgO	3.75	3.19	4.10	2.24	2.16	2.61
Na_2O	0.69	1.20	1.01	0.52	0.48	1.26
K_2O	4.88	3.21	5.10	4.77	4.86	4.62
CaO	7.14	8.68	10.33	0.79	0.80	2.45
TiO_2	0.86	0.91	0.80	1.24	1.16	0.88
P_2O_5	0.31	0.14	0.21	0.11	0.12	0.11
SO_3	0.08	0.06	0.29	0.04	0.03	0.02
Cr_2O_3	0.04	0.05	–	–	–	0.05
MnO	0.08	0.11	0.12	0.11	0.12	0.14
Co_2O_3	–	–	–	0.01	–	–
NiO	0.03	0.02	0.03	0.03	0.03	0.03
CuO	0.01	0.02	0.02	0.02	0.03	–
ZnO	0.02	0.02	0.04	0.02	0.02	0.02
Rb_2O	0.05	0.04	0.04	0.06	0.07	-
SrO	0.02	0.04	0.03	0.02	0.02	0.02
ZrO_2	0.03	0.02	0.03	0.03	0.03	0.03
SnO_2	–	–	–	–	0.34	–

While the CaO contents differ between 0.79 and 10.33 wt.%, the MgO concentrations were between 2.16 and 4.10 wt.% (Table 1). The correlation between CaO and MgO for all the samples is given in Figure 3a. There is a positive correlation between these oxides but it is not strong enough to conclude that these elements were originated from the same type of raw materials. It may be considered that the source of CaO not only comes from dolomitic materials but predominantly from the calcareous materials. There is also a negative correlation between SiO_2 and CaO (see Figure 3b). This could be explained by the tendency, that the increase in the dosage of the calcium-rich materials content resulted in the decrease in the dosage of silica-rich materials in the raw material mixture.



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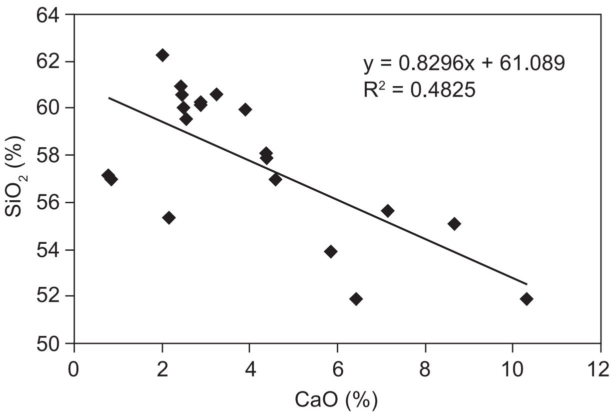


b)

Figure 3. The correlation between: a) CaO versus MgO and b) SiO_2 versus CaO for the investigated sherds.

The well known fact is, that alkaline and earth alkaline oxides may act as fluxes and promote secondary mineral formation at lower sintering temperatures. Although detected amounts of sodium in the sherds are low, the potassium contents change in a moderate range. Potassium oxide should have been supplied especially from the feldspars and illitic clays. The highest total of alkali and earth alkali amount was found in the sample M8. The variation of alkaline and earth alkaline oxides for all the samples is given in Figure 4. Non-synchronized changes of alkaline and earth alkaline oxides suggest that there is wide variety for the materials used for their production. Iron oxide ratios which were shown as Fe_2O_3 in this study change from 6.58 to 9.11 wt.% and it is the principal colorant element for the bodies.

Phase analysis of the examined sherds identified following minerals: quartz (SiO_2), plagioclase [(Na,Ca) $AlSi_3O_8$], alkali feldspar ($KAlSi_3O_8$), illite/muscovite $[(K,H_3O)Al_2Si_3AlO_{10}(OH)_2]/[(K,Na)(Al,Mg,Fe)_2(Si_{3.1}Al_{0.9})O_{10}(OH)_2]$, anorthoclase $[(Na,K)(Si_3Al)O_8]$, hematite (Fe_2O_3), calcite ($CaCO_3$), gehlenite ($Ca_2Al_2SiO_7$), and diopside $[Ca(Mg,Al)(Si,Al)_2O_6]$. The detected phases and the estimated firing temperatures of the sherds are presented in Table 2.

The presented mineralogical composition makes possible to estimate firing temperature of the sherds. This issue has previously been discussed in several studies. For example; illite/muscovite or mica structure decomposes in the interval 900-1000°C [3-5]. From the decomposition of illite, an intermediate phase originates between spinel ($MgO.Al_2O_3$) and hercynite

Table 1. XRD results and estimated firing temperatures of the investigated sherds.

Group	Code	Minerals/Phases	Experimental code	Estimated firing temperature (°C)
A	A1	quartz, alkali feldspar, plagioclase, illite/muscovite, hematite	M3, M9, M10, M11, M14	600-700
	A2	quartz, alkali feldspar, plagioclase, hematite	M5, M7, M17, M18, M20	900-1000
B	B1	quartz, alkali feldspar, plagioclase, calcite, illite/muscovite, hematite	M8, M12, M15, M16, M19	600-700
	B2	quartz, alkali feldspar, plagioclase, calcite, hematite	M6	850-900
BC	BC1	quartz, alkali feldspar, plagioclase, diopside, gehlenite, hematite	M1, M2, M13	900-1000
	BC2	quartz, alkali feldspar, anorthoclase, plagioclase, diopside, gehlenite, hematite	M4	900-1000

($FeO.Al_2O_3$) [6]. Calcite decomposition starts within 650°C and ends with the temperature at around 900°C. Dolomite has two-staged decomposition and begins at 650°C. After the decomposition of dolomite into calcite and MgO, decarbonization of complete system ends at 900°C, similar to calcite decomposition [3, 7-9]. This temperature may extend to 1100°C for calcite rich systems [10]. However, secondary calcite may occur in ceramics as a result of post-burial deposition processes due to decarbonization of lime [3, 9]. Quartz and feldspars can persist up to 1000°C [11]. Pyroxenes like diopside and augite may be generated from dolomite and silica reactions at 800-900°C. CaO is a highly reactive oxide and reacts with silica and concludes wollastonite around 850°C. Gehlenite may be formed at 850°C with the reaction of CaO and illite structure [12]. Moreover, these secondary mineral formation temperatures may be affected by firing type such as pit or kiln firing conditions. For instance, calcite decomposition ends around 825°C in kiln firing but it tends to be at around 875°C in pit firing conditions [13]. These reactions, of course, are related with the temperature, soaking time at peak temperature, abundance and the type of minerals/phases present, atmosphere, pressure, specific surface area of components, etc.

According to their mineral assemblages, the investigated samples can be grouped into three types of pottery. Group A is a cluster of illitic/micaceous and iron rich siliceous clay contents. Group B differs with its calcareous content from group A. Group BC is a mixture of these groups.

Clay deposits may include some non-plastic materials like quartz, feldspars and iron compounds. Non-plastic materials in potsherds may be within the clay or used deliberately as grog materials. The addition of grog materials such as siliceous raw materials, shells or crushed potsherds may be seen in several artifacts [11]. Grog materials may improve the mechanical properties of the pots during both shaping and firing. Especially, the addition of the calcareous materials may contribute to preserve the desired shape after forming [14].

Thermal Analysis

The firing temperatures of bodies containing high amount of clay minerals should have not exceeded the interval of 900-950°C. The bodies containing calcite or dolomite residua should have fired at temperatures below the interval of 850-900°C for decarbonizing. The bodies without clay and carbonated minerals should have reached the temperature interval of 900-1000°C during firing. The bodies containing clay minerals and/or carbonated minerals should have been exposed to lower temperatures in a range of 600-700°C. The decomposition of carbonated minerals was confirmed with TG-DTA analyses. The results of TG-DTA analyses supplied some information about the estimation of firing temperatures but the results needed also other comparative techniques. TG-DTA graphs of M8 and M20 are given in Figure 5a and b. The endothermic reaction in Figure 5a around 735°C indicates calcite decomposition of sample M8. There is not however, an indicative reaction in Figure 5b. It concludes that sample M20 has been exposed to relatively high firing temperatures.

Redox conditions of firing and total amount of iron determine the potsherds color [15]. Hematite which was observed in almost all the body samples indicates the oxidation atmosphere during firing.

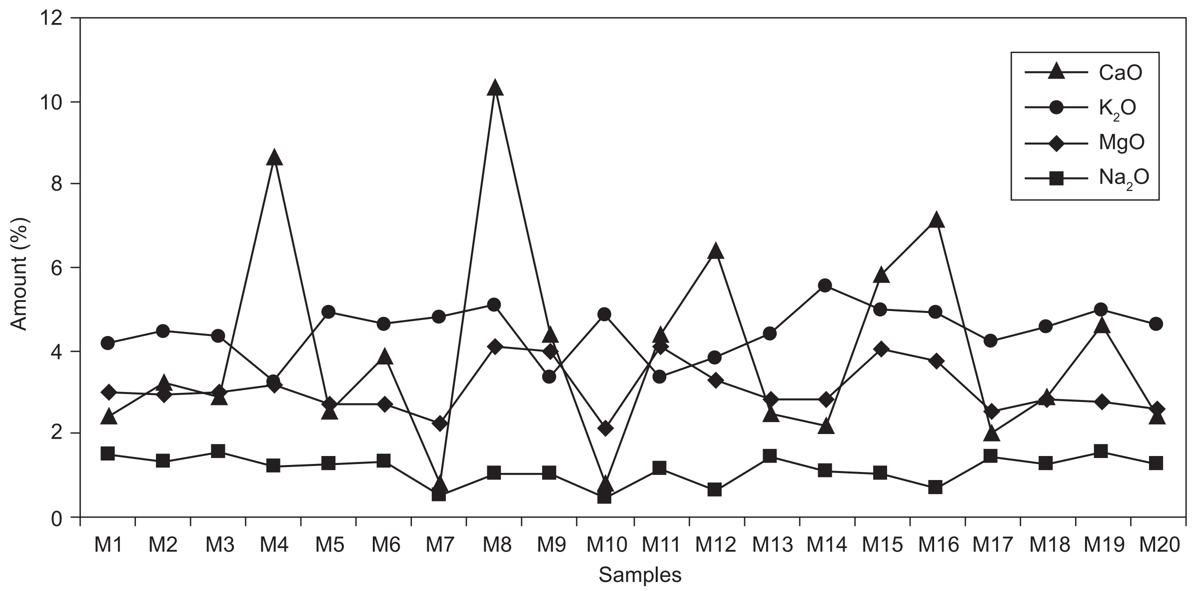
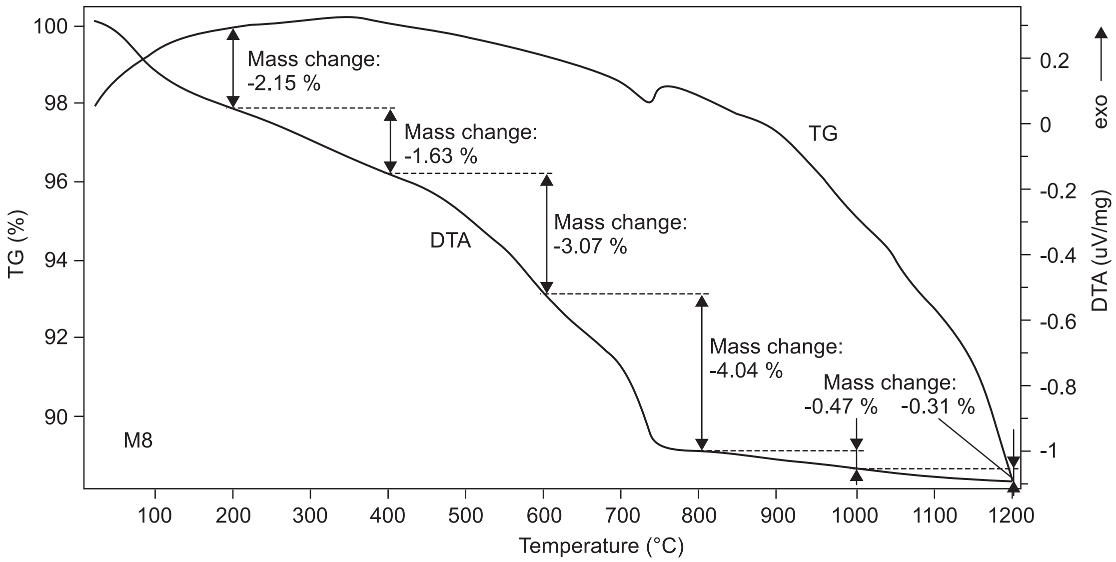


Figure 4. The variation of alkaline and earth alkaline oxides used for investigated sherds.



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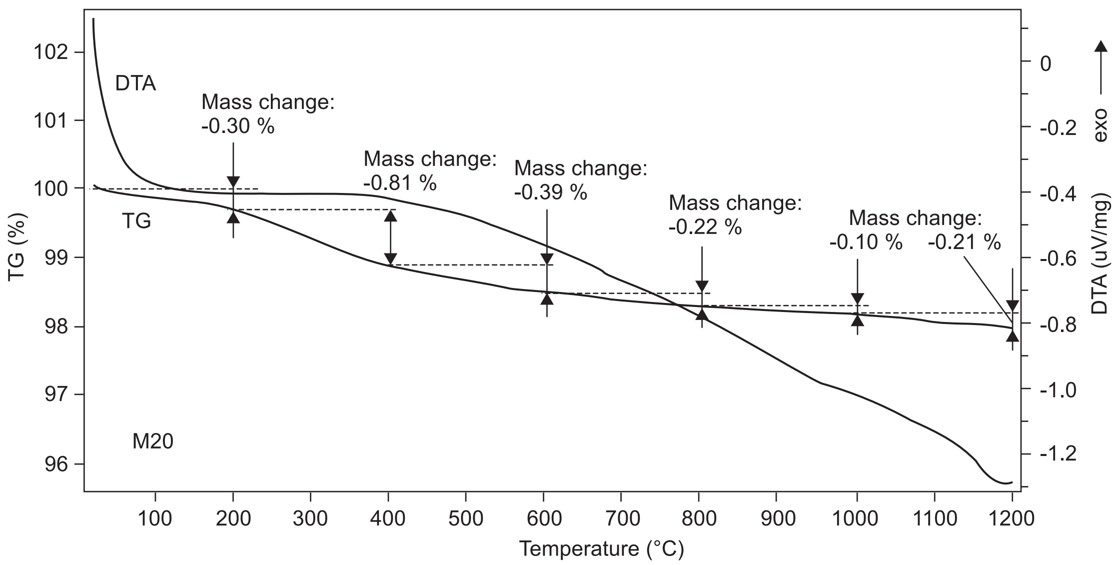


b)

Figure 5. TG-DTA graphs of sample M8 (a) and sample M20 (b).

Microstructural Analysis

The body and surface layer of the potsherds were examined by SEM and EDX. The surface layers have iron-rich compositions with various alkali contents. Back-scattered electron (BSE) images of samples M8 and M16 and semi-quantitative EDX analysis results of their slip layers were given in Figure 6. The surface layer of sample M8 has the lowest and sample M16 has the highest iron content among all of the samples.

It has been noticed that the surface layers of the potsherds still stand even though they had been exposed to several principally climatic and hot-cold cycles through more than 2000 years. Producing such a durable coating layer should not be random. These surface layers should also have similar compatible expansion coefficients with the underlying bodies because almost all the surface layers have no cracks or spalling. The thickness of surface layers on individual bowl change from 5 to 30 μm having almost constant thickness through the whole surface of each body. They most probably should have been applied to body surfaces in the form of suspension. They have nearly the same elemental composition but exhibit differences in color. It shows that the redox conditions of the kilns were adjusted [16, 17]. It has been already known that monochrome and bichrome coatings were produced through a single firing cycle consisting of a sequence of oxidizing and reducing steps obtained by varying the firing atmosphere for ancient Greek ceramic wares [17, 18]. The similar chemical and physical characteristics for the Megarian bowls from Dorylaion may be considered as a part of the continuity of this tradition.

By increasing firing temperature, some interactions occur in the structure of clay based systems. Some of these interactions can be described as welding behavior between the clay matrix and grains, shape changes of mineral phases, an increase of the aggregation rate within the clay matrix with the formation of secondary porosity and intergranular bridges [19]. The investigation of the potsherds at different magnification gave some detailed information about the microstructural characteristics. It is clear that there is a progressive welding behavior between clay matrix and grains related to maximum firing temperature in the SEM image of sample M1 (Figure 7).

These changes may become more evident in a cal cium rich sample than the siliceous sample at lower temperatures. Rounded pores in a siliceous micro-structure as shown in Figure 8 should be considered as the predominant indications of the improved degree in sample M5.

Lower sintering temperature should not have made an impressive change like in the microstructure of M9 sample given in Figure 9.

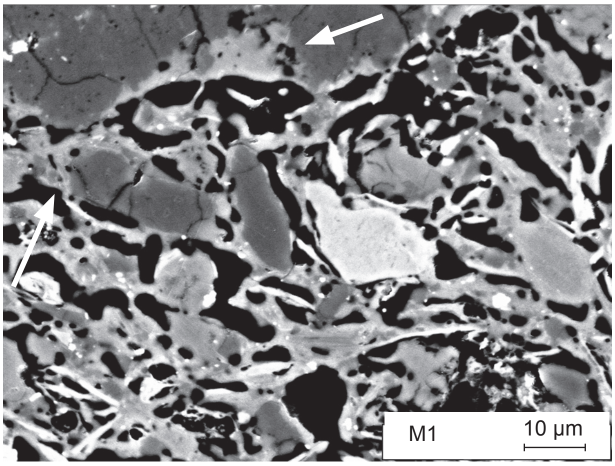
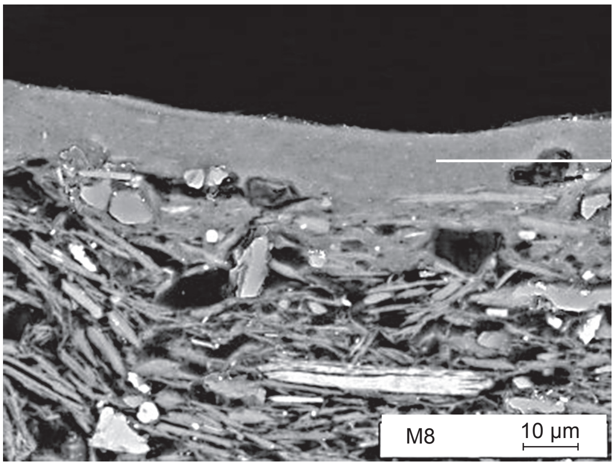
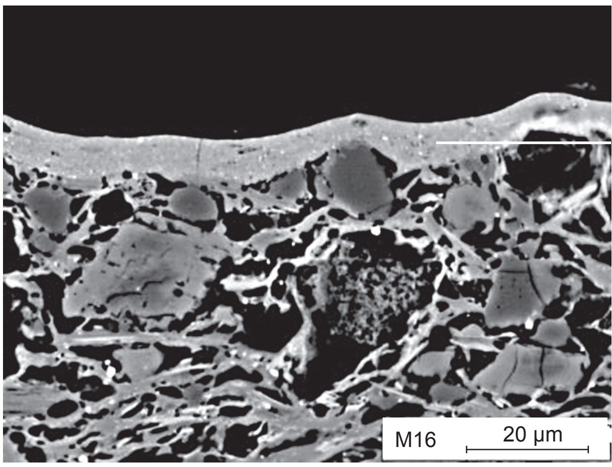


Figure 7. A back-scattered SEM image of sample M1 showing welding behavior between clay matrix and grains related with the peak firing temperature.



M8	
Oxide	wt. %
SiO_2	48.60
Al_2O_3	34.00
Fe_2O_3	8.32
MgO	2.83
Na_2O	1.33
K_2O	3.30
CaO	0.94
TiO_2	0.68



M16	
Oxide	wt. %
SiO_2	52.07
Al_2O_3	27.48
Fe_2O_3	13.65
MgO	1.65
Na_2O	0.25
K_2O	3.36
CaO	1.11
TiO_2	0.44

Figure 6. Back-scattered SEM images of M8 and M16 samples in cross-section and semi-quantitative EDX results of surface layers of M8 and M16 samples.

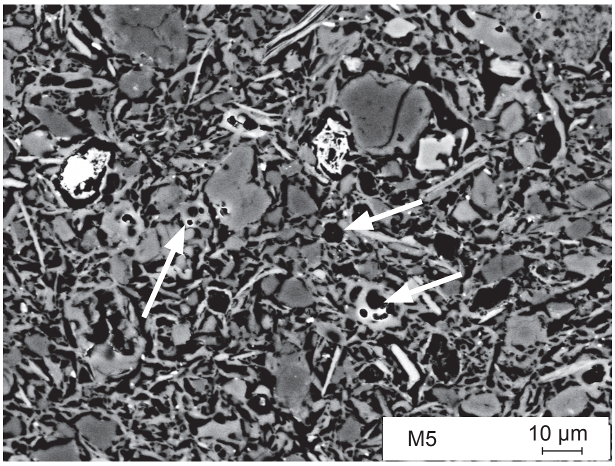


Figure 8. Predominantly rounded pore structures in the back-scattered SEM image of the sample M5.

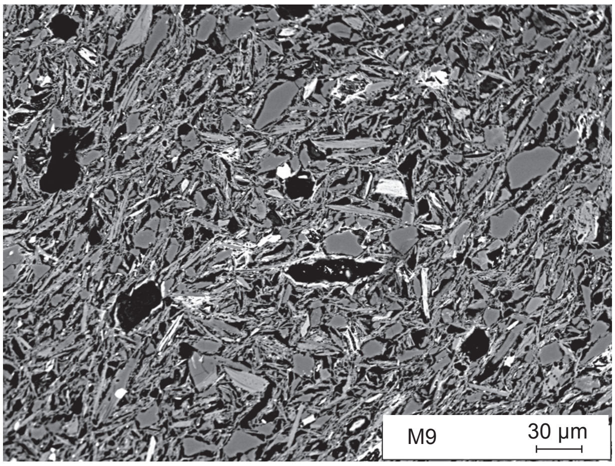


Figure 9. A back-scattered SEM image of M9 sample deduced from lower sintering temperature than the others.

CONCLUSION

The presented study has a frame of a contribution to enlighten the technological aspect of the pottery production of some Hellenistic wares excavated in Dorylaion. The characterization performed by different experimental techniques indicated that ceramic bodies were produced with different raw materials including carbonated and siliceous clays and probably coated with iron rich suspension coatings. It was showed that these ceramic wares were exposed to different firing temperatures and atmospheres. It should be noticed that the ceramic technology in the Hellenistic period showed elevated level making products containing up today almost no cracks or spalling. The results of this study may contribute to the comparison of the pottery making technology in the other Hellenistic period settlements.

Acknowledgment

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